

Leaching of U(VI), Am(III), and Sr(II) from Simulated Tank Waste Sludges

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ABSTRACT

Using a series of acidic, alkaline, and complexant solutions, the leaching behavior of U(VI), Am(III) and Sr(II) from synthetic sludges was studied and compared with previously reported results on the behavior of plutonium. Spectroscopic techniques, including EXAFS and NMR, were used to help interpret the leaching behavior. Considerable amounts of U(VI) were removed from the sludges by 3 M NaOH and the leaching of americium by 3 M NaOH was enhanced in the presence of strong oxidants at elevated temperatures. These observations are discussed in terms of actinide speciation in alkaline solutions and expected to have significant impact on the development of the strategies for tank waste sludge washing.

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INTRODUCTION

Large-scale separations of metallic species using solvent extraction methods always have the associated generation of liquid effluents, some of which must ultimately be considered as wastes. Hence, a full description of the separations science (and technology) of hydrometallurgical separations must always include an element of waste treatment and disposal. This is particularly true for the processing of nuclear fuels. The effluents from solvent extraction separations of nuclear materials typically contain not only radioactive byproducts (fission products, minor actinides, activation products), but hazardous chemicals as well. Most, but not all, of the fission products are metals. To accommodate the nature of the aqueous effluents produced in plutonium production and uranium recovery, underground storage tanks are the preferred method for storage of these byproducts. Underground storage is desirable because the fission products remain intensely radioactive (about 6 MCi for each ton of spent fuel 1 year after discharge from the reactor) for decades. The soil surrounding the tank provides shielding to assist in reducing unnecessary operator exposure. It was also conceived as a barrier to migration of the radionuclides from the tanks to the surrounding environment.

At present, large quantities of nuclear wastes from decades of plutonium production within the U.S. weapons complex are stored in underground tanks that are made of either carbon steel or stainless steel. To reduce the corrosion of the tank material and to minimize the concentration of metallic fission products and actinides in the liquid effluents, the originally acidic waste streams were made basic by adding large quantities of sodium hydroxide.^[1-3] After a few decades of storage, the tank wastes are primarily composed of supernatant liquid, salt cake, and solid sludge. The majority of the radionuclides are known to be in the sludge, which makes the sludge the largest source of high level wastes (HLW). The HLW will be vitrified and converted to borosilicate glass in canisters for storage and disposal.^[4] This is a very expensive process—the cost is estimated to be about \$1 million for each canister of vitrified HLW.^[5] As a result, there is an urgent need for sludge pretreatment to reduce the volume of HLW to be vitrified so that a major cost reduction in the HLW disposal can be achieved.

The baseline sludge pretreatment strategy includes retrieving the sludge by sluicing and pumping with inhibited water (0.01 M NaOH/0.01 M NaNO₂), leaching the sludge with caustic solution (3 M NaOH), then washing the sludge with inhibited water to remove the added NaOH and the components dissolved during the caustic leaching step.^[6,7] In addition, alkaline oxidative leaching is also proposed for the removal of some problematic elements (e.g., chromium) from the tank sludges.^[8,9] Ideally, these processes should significantly remove

the nonradioactive components but minimize the dissolution of actinides and other radioactive materials from the sludge so that the leaching solutions and the leached sludge can be handled as low level waste (LLW) and HLW, respectively. However, preliminary sludge leaching tests indicated that, while the removal of certain nonradioactive components (e.g., chromium) was not as efficient as expected, the dissolution of some actinides (e.g., plutonium) was actually enhanced during the caustic washing.^[9] These unexpected results could significantly affect the decision on the pretreatment strategies and suggest that the chemical behavior of actinides during caustic leaching is not adequately understood. Currently, there are few available data on the leaching of actinides under alkaline conditions.^[10] The majority of the data in the literature are obtained under acidic conditions.^[11]

To help design and optimize the flow sheets for the pretreatment of tank sludges, we have started a comprehensive study of the chemical behavior of actinides during caustic leaching. Simulated sludges were prepared according to the historical processes for reprocessing nuclear spent fuels (Bismuth Phosphate, Redox and PUREX processes). Radionuclides, including uranium, neptunium, plutonium, americium, and strontium, were incorporated into the simulated sludges under conditions relevant to the tank supernatant solutions. Spectroscopic techniques, including extended x-ray absorption fine structure (EXAFS), were used to characterize the sludges loaded with radionuclides. The leaching behavior of the radionuclides was studied using a variety of leaching solutions. The results for plutonium^[10] and neptunium^[12] have been presented in previous publications. This article summarizes the results for uranium, americium, and strontium.

EXPERIMENTAL

Chemicals

All chemicals were reagent grade or higher. Distilled water was used in preparations of all the solutions. Radioactive tracers, ²³³U and ²⁴³Am, were obtained from the inventory at Lawrence Berkeley National Laboratory and purified by ion exchange. Analysis by α -spectroscopy indicated that the purified americium contains 94% ²⁴³Am and 6% ²⁴¹Am and the purified uranium contains 96.6% ²³³U and 3.3% ²³²U. Radiochemically pure ⁹⁰Sr solution was purchased from Pacific Northwest National Laboratory and used without further purification. For the experiments with macroamounts of uranium, depleted UO₃(s) or UO₂(NO₃)₂·4H₂O(s) were used to prepare the stock solution.

For the NMR experiments, ^{13}C -labeled oxalic acid (oxalic-1,2- ^{13}C) and malonic acid (malonic-1,3- ^{13}C) were purchased from Cambridge Isotopes (99% ^{13}C).

Sludge Preparation

Four simulated sludges (BiPO_4 , modified BiPO_4 , Redox, and PUREX) were prepared at Argonne National Laboratory based on the process history and the published procedures,^[2] except as noted here. All the simulated sludges were prepared without the addition of radioactive materials except for the Redox sludge, in which 0.45% (by weight) depleted uranium was incorporated during the preparation. To prepare the simulated BiPO_4 sludges, two thirds of the lanthanum in the published recipe^[2] were substituted with equal amounts of neodymium and europium to allow the use of more spectroscopic techniques to characterize the sludges. The wet sludges were stored in tightly capped containers without being exposed to air for any lengthy period of time prior to use. A portion of each sludge simulant was dried in an oven at 120°C until a constant mass was achieved. Both wet and dry sludges were used in the leaching experiments. Details of the synthesis and analysis by electron scanning microscopy (SEM) and energy dispersive spectroscopy (EDS) have been presented elsewhere.^[13]

Radionuclides, including depleted uranium, ^{233}U , ^{243}Am , and ^{90}Sr , were loaded onto the sludge from a solution of 0.10 M Na_2CO_3 /0.50 M NaOH /1.0 M NaNO_3 . This solution, called the "supernatant simulant," simulates the conditions of the supernatant in the waste storage tanks. Twenty milligrams of the sludge were shaken with 1.0 mL supernatant simulant containing appropriate amounts of the radioactive materials for 15 to 24 hours. For the tracer level experiments, usually about 1000 to 10,000 Bq ^{233}U , ^{243}Am , or ^{90}Sr were loaded onto the 20 mg of sludges. In the oxidative leaching experiments with americium, more radioactive materials were used to achieve better statistics in counting ($\sim 8.3 \times 10^4$ Bq ^{243}Am in 100 mg sludge). For the experiments with macro amounts of uranium, about 0.5% (by weight) depleted uranium was loaded onto the sludges from the supernatant simulant. Consequently, in these experiments, the BiPO_4 , modified BiPO_4 , and PUREX sludges contained 0.5% (by weight) uranium. The Redox sludge contained a total of 0.95% (by weight) uranium, among which 0.45% was incorporated during the sludge preparation and 0.5% was loaded after the sludge had been prepared through sorption or precipitation from the supernatant simulant.

Leaching Procedures

Previous leaching experiments with plutonium were conducted in a consecutive mode with seven solutions ranging from alkaline to acidic. The solutions are: 0.01 M NaOH/0.01 M NaNO₂, 3.0 M NaOH, H₂O, 0.05 M glycolic acid/0.1 M NaOH, 0.1 M HNO₃, 2.0 M HNO₃ and 0.50 M HEDPA (1-hydroxyethane-1,1-diphosphonic acid). The percentage of leached plutonium in each step was calculated based on the residual plutonium in the sludge after the previous leaching step.^[10] The same solutions were used in the present study of uranium, americium, and strontium. However, the leaching experiments were conducted in a parallel mode, that is, each leaching solution was contacted with "fresh" sludge loaded with the same amount of radionuclides. The parallel leaching mode made it possible to evaluate the leaching efficiency of each solution independently and reduced the uncertainty in the calculation of the leaching efficiency when there was significant loss of the sludge matrix in the consecutive leaching steps.

Two milliliters of the leaching solution was added to the 20 mg sludge loaded with radionuclides. The suspension was shaken for at least 15 hours. Kinetic experiments indicated that a steady state was reached within this period of time. Then the suspension was centrifuged and filtered with Millex-HV Filter (0.45 μ m). An aliquot of 100 μ l solution was taken for radiometric assay. Comparison between the filtered and unfiltered samples indicated that, in general, centrifugation alone was effective to separate the solution from the solids for all the alkaline systems. Only in the dilute nitric acid (0.1 M) leaching, the concentration of uranium in the filtered samples was about 10–30% lower than the unfiltered samples, suggesting that colloidal materials are likely to form during the dilute nitric acid leaching of uranium.

To study the effect of radiation on the leaching behavior of actinides, a few sludge samples loaded with uranium were irradiated with a 600 Ci ⁶⁰Co source (Model Gammabeam 150C, Nordion International Inc.). Sludge samples were sealed in polyethylene vials and irradiated for different durations of time prior to the leaching experiments. The dosage each sludge sample received was calculated from the source intensity, the distance from the source, and the duration of time.

Analytical Techniques and Instrumentation

The α -activity of ²³³U and ²⁴³Am and the β -activity of ⁹⁰Sr were measured by liquid scintillation counting on a Perkin Elmer liquid scintillation counter (Model 1214/1219). EcoLume was used as

the scintillation solution. The isotopic purity of ^{233}U and ^{243}Am in the stock solutions was checked with an α -spectrometer (Model TENNELEC TC 256/257).

The concentrations of depleted uranium were determined by fluorimetry^[14,15] on a SPEX Fluoro Max-2 fluorometer (ISA Inc.). The intensity of the fluorescence emission of U(VI) at 516 nm was measured with the excitation at 330 nm. Standard solutions of U(VI) (10^{-7} to 10^{-4} M) in 1 M H_3PO_4 were used for calibration. In this range, the fluorescence intensity at 516 nm was proportional to the concentration of U(VI) in 1 M H_3PO_4 . For analyzing unknown samples, a small volume of the sample (usually 0.1 mL) was mixed with 3 mL 1 M H_3PO_4 and the fluorescence intensity at 516 nm was measured. To reduce the matrix effect and check the reliability of the results, the method of standard addition was used.^[14]

EXAFS was used to characterize the uranium incorporated into the sludges. The uranium L3- or L2-edge spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on the wiggler beamline 4-1 under normal ring operating conditions (3.0 GeV, 50–10 mA). The EXAFS data were collected in the transmission mode (using argon-filled ionization chambers) up to $k \sim 16 \text{ \AA}^{-1}$. Four or more scans were performed for each sample. The EXAFS data were processed using the R-space X-ray Absorption Package (RSXAP).^[16]

^{13}C -NMR experiments were performed on the 400 MHz Bruker AMX Spectrometer VBAMX-400 of the NMR Laboratory, Chemistry Department, University of California at Berkeley. 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt was used as the internal standard.

RESULTS AND DISCUSSION

Characterization of Uranium in the Sludges

Figure 1 shows the Fourier transform magnitude of the EXAFS spectra for U(VI) in the simulated sludges. The data for U(VI) hydroxide precipitated from alkaline solutions are also shown for comparison. The complexity of the sludge compositions and the lack of standard compounds do not permit a detailed analysis of the coordination environment of U(VI) in the sludges. However, a qualitative comparison between the sludges and the reference material can be made. Data in Fig. 1 indicate that the chemical environments of U(VI) in the four simulated sludges are different. All the spectra, except that for the Redox sludge, are significantly different from that for uranyl hydroxide. This implies that U(VI) is probably incorporated into the BiPO_4

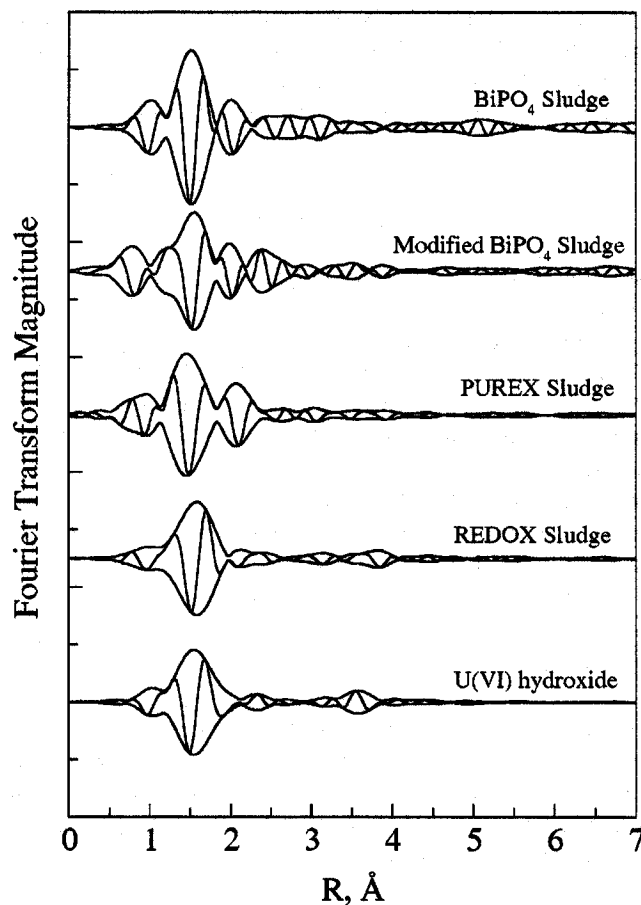


Figure 1. EXAFS Fourier transform magnitude of the U(VI) in the synthesized sludges.

and PUREX sludges, rather than being precipitated as hydrolysis products on the sludges.

As shown in Fig. 1, the spectrum for the Redox sludge is quite similar to that of uranyl hydroxide. At present, it is not clear whether the U(VI) in the Redox sludge exists in the form of hydroxide (or hydrous oxide) or is associated with aluminate, a principal component in the Redox sludge.^[2] Attempts were made to prepare uranyl aluminate and compare its EXAFS

spectra with those for the Redox sludge and uranyl hydroxide. However, the results were inconclusive. Further EXAFS studies with well-prepared reference compounds are needed to provide insight into the chemical environments of the U(VI) in all the four simulated sludges.

Leaching Behavior

Comparison Between Dry and Wet Sludges

Comparative experiments using dry and wet sludges were performed with ^{233}U tracer. The leaching behavior of $^{233}\text{U(VI)}$ from the dry and wet sludges was found to be very similar for all the four sludges. A representative comparison between the dry and wet BiPO_4 sludges is shown in Table 1.

These results imply that the sorption property of the simulated sludges was not altered during the sludge drying process (at 120°C). In the later experiments, only dry sludges were used.

Effect of Radiation

Sludge samples loaded with depleted uranium were irradiated by ^{60}Co to total doses of 7×10^5 or 5×10^7 rad in a period of ten days. Leaching experiments were conducted in comparison with the control samples without being irradiated. No significant effect of radiation on the leaching behavior of uranium was observed at these dose levels.

Table 1. Percentages of $^{233}\text{U(VI)}$ leached from the BiPO_4 sludge.

Leaching solution	0.01 M NaOH	3 M NaOH	H_2O	0.1 M NaOH	0.1 M HNO_3	2 M HNO_3	0.05 M HEDPA
	0.01 M NaNO_3 (%)			0.05 M Glycolic acid (%)			
Dry sludge	0.2	11	0.3	0.3	60	95	100
Wet sludge	0.4	8	0.2	1	33	99	96

Acidic Leaching (0.1 M or 2.0 M HNO₃)

The results of the two acidic leaching processes for all the four sludges are quite similar. High percentages of uranium, americium, and strontium were found in the acidic leaching solutions: for uranium, 30–96% by 0.1 M HNO₃ and 70–100% by 2.0 M HNO₃; for americium, 70–100% by either 0.1 M or 2.0 M HNO₃; for strontium, 72–90% by either 0.1 M or 2.0 M HNO₃. Significant dissolution of the sludge matrix materials in the acidic leaching was also observed (up to 94% by weight). The high percentage of the leaching of radionuclides is well correlated with the weight loss of the sludge and the concentrations of the nonradioactive constituent elements in the leaching solutions. The previous study demonstrated the correlation with the concentrations of Cr, Nd, Mn, and Fe.^[10] Fluorescence measurement experiments in this study also demonstrated that the concentration of uranium in the acidic leaching solutions of BiPO₄ sludges correlated with the concentration of europium mobilized from the sludges. The europium was purposely added to the BiPO₄ sludges during the sludge preparation to allow the use of more characterization techniques including fluorescence spectroscopy.

In contrast to uranium, americium, and strontium, the percentage of plutonium leached from the sludges by nitric acid is much lower, ranging from 2% to 20% for most of the samples.^[10] These results suggest that the uranium, americium, and strontium in the sludge are more accessible to acid leaching than plutonium. It is likely that the plutonium in the sludges has become rather intractable through more extensive hydrolysis and polymerization during the sludge preparation. The best available information in the literature indicates that the most stable hydrolytic species of plutonium is PuO₂, for which log K_{sp} is reported to be in the range of –52 to –61.^[11]

Leaching with H₂O or Weak Base (0.01 M NaOH/0.01 M NaNO₂, H₂O or 0.05 M Glycolic Acid/0.1 M NaOH)

As Table 2 shows, the leaching percentages of uranium, americium, and strontium from all the four sludges are generally less than 1%, except for the uranium leaching from the Redox and PUREX sludges (up to 16% for PUREX and 24% for Redox sludges). These percentages correlate with the relative aluminum contents of the two sludges.

Table 2. Percentages of ^{238}U , ^{243}Am , and ^{90}Sr leached by H_2O and weak base solutions.

	H_2O (%)			0.01 M NaOH 0.01 M NaNO_3 (%)			0.1 M NaOH 0.05 M Glycolic acid (%)		
	U	Am	Sr	U	Am	Sr	U	Am	Sr
BiPO_4 sludges	~0	0.1	0.1	0.2	0.2	0.9	0.3	0.3	0.4
Modified BiPO_4 sludges	0.5	0.1	0.1	0.2	0.2	0.1	0.4	0.3	0.1
Redox sludges	8	0.2	0.2	3	0.5	0.9	7	0.4	0.4
PUREX sludge	20	0.4	0.4	5	0.3	1.3	12	0.5	0.3

Leaching with Strong Base (3 M NaOH)

Results indicate that significant amounts of uranium were leached from the sludges by 3 M NaOH (15–90%), but only minimal amounts of americium or strontium (0.3–0.9%) were leached by 3 M NaOH. The higher percentages of uranium by 3 M NaOH could be attributed to the formation of anionic uranyl species (e.g., $\text{UO}_2(\text{OH})_3^-$) in strongly basic solutions.

In addition, a significant difference was found between ^{233}U tracer and macro amounts of depleted uranium in the 3 M NaOH leaching from Redox and PUREX sludges. For these two sludges, 82–89% of ^{233}U was found in the 3 M NaOH leaching, while only ~15% of depleted uranium was found in the same leaching (corresponding to an approximate solubility limit of $\sim 2 \times 10^{-5}$ M U in 3 M NaOH). This difference suggests that different mechanisms may be involved in the leaching at tracer and macro levels. Sorption/desorption was probably the process at the tracer level, while precipitation/dissolution was the major process at the macro level. With macroscopic concentrations of uranium present, it is more likely that the concentration of uranium is controlled by the solubility of uranyl solids in the sludge. At present, we do not know what uranyl solid phases exist in the simulated sludges. However, based on the available thermodynamic data on uranium hydrolysis, the dominant U(VI) species in concentrated sodium hydroxide solutions is likely to be anionic species such as $\text{UO}_2(\text{OH})_3^-$.^[17]

In contrast to uranium, no difference in the percentage of strontium leached from the four sludges by 3 M NaOH was observed between the tracer (^{90}Sr only) and the macro (^{90}Sr + stable strontium carrier) experiments. Without information on strontium speciation, we can only postulate that

the strontium in the sludges could be incorporated in phosphate, aluminate or silicate phases, or present as hydrous oxide ($\text{SrO} \cdot x \text{H}_2\text{O}$) or carbonate (SrCO_3)—both (especially the latter) having low solubilities in alkaline solutions.

Leaching with Complexants

0.5 M HEDPA

As shown by Table 3, uranium and strontium were almost completely mobilized by 0.5 M HEDPA from the four sludges. The mobilization of americium was complete by 0.5 M HEDPA from the Redox and the PUREX sludges, but only 45–60% from the BiPO_4 sludges. In general, the high percentages of leaching by HEDPA are probably due to the high stability of the HEDPA complexes with the radionuclides and the sludge matrix components.^[10] The lower percentages of americium leaching from the BiPO_4 sludges are consistent with the well-known behavior of BiPO_4 to coprecipitate trivalent/tetravalent actinides. In Table 3, the results from the previous study on plutonium are also listed for comparison. Again, these data indicate that the plutonium in the sludges is more intractable than uranium, americium, or strontium.

Oxalic Acid

Leaching of uranium by oxalic acid from the Redox sludge was performed over a wide pH range (2–12). Figure 2a compares the

Table 3. Percentages of ^{238}U , ^{243}Am , ^{90}Sr , and ^{238}Pu leached by 0.5 M HEDPA.

	U (%)	Am (%)	Sr (%)	Pu ^a (%)	
				Pu(III/IV) ^b	Pu(VI) ^b
BiPO_4 sludge	98	60	86	8.5	15.9
Modified BiPO_4 sludge	95	45	95	3	13
Redox sludge	98	100	100	<0.4	<0.4
PUREX sludge	100	98	99	<0.4	<0.4

^a Results from Ref.^[10]

^b The initial oxidation states of plutonium.

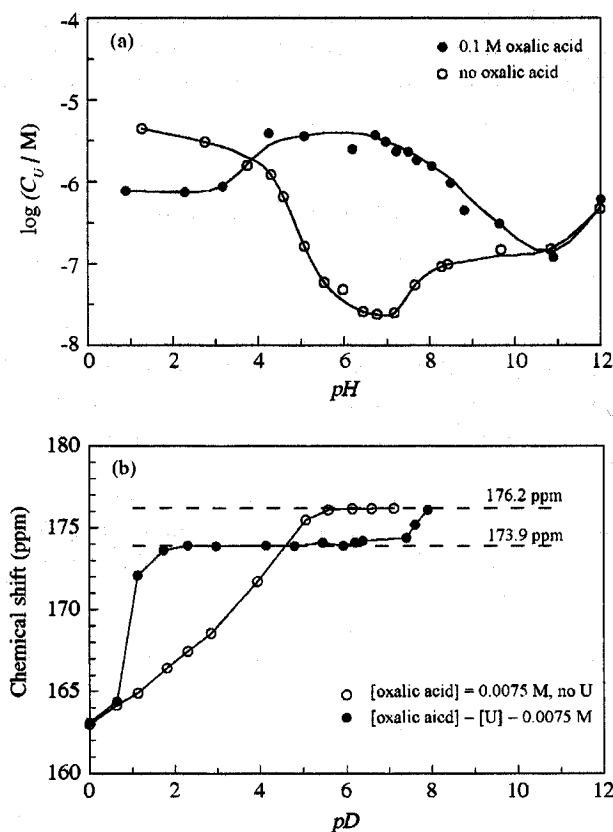


Figure 2. (a) The concentration of U(VI) leached from the Redox sludge as a function of pH. Sample conditions: 10 mL, 50 mg Redox sludge containing 0.45% (wt) of ^{238}U , $I = 1.0\text{ M NaNO}_3$. (b) Chemical shifts of the carbon in oxalic acid as a function of pD.

concentrations of uranium in the absence and presence of oxalic acid. In the absence of oxalic acid, the dissolution of uranium from the sludge decreases as the pH is increased from 2 to 7, which is understandable because the hydrolysis and precipitation of uranium would inhibit its mobilization from the sludge. When the pH is further increased from 7 to 12, the uranium concentration increases probably due to the formation of anionic uranyl hydroxyl species [e.g., $\text{UO}_2(\text{OH})_3^-$]. The presence of 0.1 M oxalic acid results in significantly more uranium mobilized from the sludge in the pH range from 4 to 9, but shows little effect when the pH is above 10.

To help interpret the leaching data and provide insight into the competition between complexation and hydrolysis, ^{13}C NMR experiments were conducted with oxalic acid in the absence and presence of uranium. The results are shown in Fig. 2b. In the absence of uranium, the observed chemical shift of the carbon atom in oxalic acid (the average δ for all the species) increased gradually from 163.0 ppm to 176.2 ppm as the pD ($= -\log[\text{D}^+]$) was increased from 0 to 7, reflecting the gradual deprotonation of oxalic acid. The "limiting shift" ($\delta = 176.2$ ppm) was assigned to the fully deprotonated oxalate species. In the presence of uranium, the chemical shift for the complexed oxalate was found to be 173.9 ppm. The NMR results indicate that the complexation of uranium with oxalate could effectively suppress hydrolysis up to pH ~ 8 . However, as the pH is further increased, the tendency of hydrolysis becomes strong and anionic uranyl hydroxyl species (e.g., $\text{UO}_2(\text{OH})_3^-$) forms. As a result, oxalate is released, as suggested by the change of the observed chemical shift from 173.9 ppm to 176.2 ppm. These data are in general agreement with the leaching results in the pH region from 4 to 12. It is worth noting that the presence of oxalic acid in the pH region from 2 to 4 results in lower concentrations of uranium than in the absence of oxalic acid (see Fig. 2a). This is probably due to the low solubility of uranyl oxalate in this pH region. Our investigations of Np(V, VI, VII) chemistry in

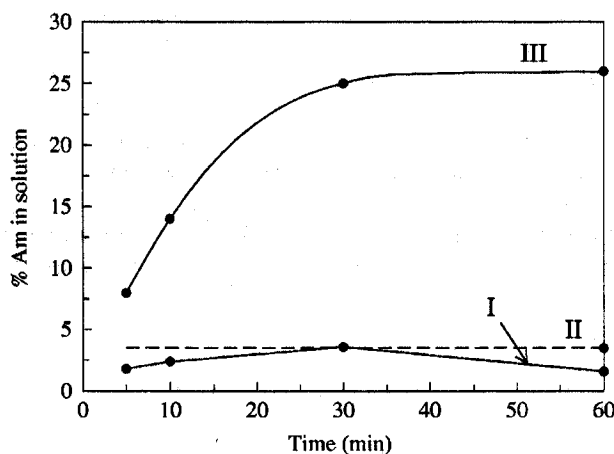


Figure 3. Oxidative leaching of americium by $\text{K}_2\text{S}_2\text{O}_8$ (0.2 M). Total americium on 100 mg BiPO_4 sludge: 8.3×10^4 Bq. (I) in the supernatant simulant (pH = 9) at 95°C; (II) in 3 M NaOH at 20°C; (III) in 3 M NaOH at 95°C.

sodium or lithium carbonate/hydroxide solutions confirm that solution phase speciation in strongly basic media containing complexing ligands can be quite complex.^[12]

Leaching with Oxidants

Data in Fig. 3 indicate that oxidative leaching with $K_2S_2O_8$ had a measurable effect on the mobilization of americium from the $BiPO_4$ sludge, especially in 3 M NaOH at elevated temperatures. This result may suggest partial oxidation of Am(III) to Am(V) by $K_2S_2O_8$. Such alterations in the speciation of americium will be a concern if oxidative leaching for enhanced removal of chromium from the sludges is pursued.^[8,9] It also implies a higher probability for solubilization of Pu(IV) and Np(V) since they are easier to be oxidized than Am(III).

CONCLUSION

In general, uranium(VI), americium(III), and strontium(II) in the four synthetic sludges are more susceptible to leaching than plutonium by acidic, alkaline and complexant leaching processes. Acidic leaching with 0.1 M or 2.0 M HNO_3 removed 30–100% uranium, americium, and strontium, accompanied by partial dissolution of the sludge matrix. Considerable amounts of uranium was solubilized by 3 M NaOH, probably due to the formation of anionic uranyl hydroxyl species. Only minimal amounts of americium or strontium were leached by 3 M NaOH. However, the leaching of americium by 3 M NaOH was significantly enhanced in the presence of $K_2S_2O_8$ at elevated temperatures, implying the possibility of the oxidation of Am(III) to Am(V) in strongly alkaline solutions. Strong complexants including HEDPA and oxalic acid could solubilize uranium, americium, and strontium and the extent of solubilization depends on the nature of the sludges and the competition with hydrolysis.

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